REACTIVE SILICATE COATINGS FOR PROTECTING AND BONDING REINFORCING STEEL IN CEMENT-BASED COMPOSITES

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ABSTRACT

Reinforced concrete (RC) is the major construction material for hardened structures for the Army. As a basis for shelters and for infrastructure reinforced concrete has two drawbacks; the bond between the concrete and its steel reinforcement at the interfacial zone is typically very weak and the increased porosity of the interfacial zone can accelerate penetration of chloride ions to the surface of the embedded steel reducing the time to the initiation of corrosion. Corrosion products from steel occupy a larger volume that the steel that has oxidized. The increase in volume cracks the concrete around the reinforcement and weakens the steel members. When the steel is separated from the surrounding concrete the carrying capacity of the RC structure is compromised.

A novel coating that is based on a hydraulically reactive silicate cement blended with a glass enameling frit and fused onto the steel reinforcement has been developed that addresses both the problem of bonding and corrosion. Research has been undertaken to develop basic understanding of how this composite coating performs has shown that when portland cement is used as the cementitious component in the enamel, the hydration reaction that occur in cement paste can be observed taking place in the cement attached to the glassy enamel coating. Grains of reactive calcium silicate that are embedded in the glass hydrate if exposed to water. If the glass fractures the coating is sealed by calcium silicate hydration products from the embedded cement in a "self-sealing" reaction.

1. INTRODUCTION

Extensive research as been done on characterizing the interface between concrete and embedded steel (Page, 1982; Al Khalaf and Page, 1979, Bentur, Diamond and Mindess, 1985; Wei, Mandel and Said, 1986; Horne, Richardson and Brydson, 2007). Most research have concluded that the interface or interfacial transition zone (ITZ) consist of a layer of calcium hydroxide platelets on the surface of the steel and a weak layer of calcium silicate hydrate (CSH) paste that transitions into a denser layer of paste in the adjacent concrete (Fig. 1). An interfacial transition face will form around any impermeable material embedded in the fresh cement paste. As cement paste hydrates it consolidates and excess water saturated with calcium hydroxide accumulates at the interface. The calcium hydroxide precipitates out of solution and any excess water increases the porosity of the surrounding paste, reducing its strength.
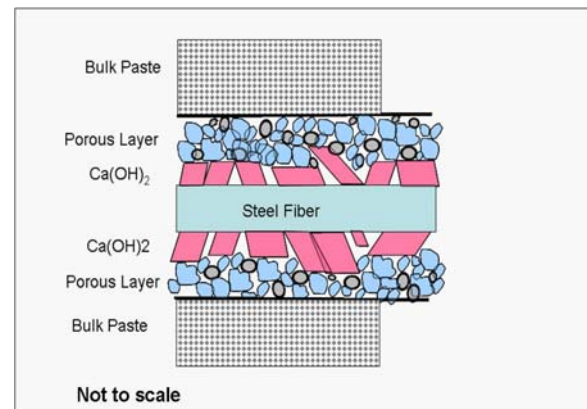
Fig. 1. Diagram showing structure of the interfacial transition zone around a steel fiber. (after Bentur, Diamond and Mindess, 1985.)

The ITZ is typically on the order of 100μm in thickness and the exact proportion of calcium silicate hydrate gel in the porous layer and the character of the calcium hydroxide layer may vary with the age of the paste (Liao et al., 2004). The maximum porosity of the ITZ is approximately three times higher than the matrix or bulk paste. The rate of chloride migration is estimated to be approximately 2.8 times faster in the ITZ than in the bulk paste.

The effect of the ITZ is to make the paste at the surface of steel weaker, more permeable and more

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hydroxide rich. The abundance of hydroxide as suggested to some researchers that the existence of the ITZ may extend the time to the onset of corrosion in the steel by maintaining a high pH to passivate the steel surface. The increased permeability however allows chloride to move rapidly along the surface of the steel and chloride speeds corrosion (Yang and Cho, 2005).

The ultimate solution to the interface problem is to replace the ITZ with dense glass enamel that contains a hydrating component like portland cement that can react with and remove the excess water (Lynch et al., 2007; Hock et al., 2008). This research is directed at examining the changes in the composition of a reactive glass enamel layer that alters the structure of the steel-concrete interfaces and determining the extent to which it can be useful in maintaining protection and preventing corrosion of reinforcing steel and improving the concrete-to-steel bond.

Research done on the use of porcelain enamel as at interface using smooth mild steel rods has demonstrated that the a glass enamel coating without a reactive silicate component does not produce a significant increase in bond strength (Table 1). With the reactive component present the bond strength increases two to three times that observed with bare uncoated steel (Hackler, Koenigstein and Malone, 2006). As the bond strength increases the fracture surface appears in the surrounding concrete, not at the interface. The strength of the composite becomes a function of the strength of the concrete.

Research to date indicates that the hydration of the reactive silicate in the coating removes the "wall effect" that creates the ITZ. Without the ITZ, there is a continuous cementitious bond between the glass layer fused to the steel and the surrounding concrete or mortar. The hydration of the cement produces calcium silicate hydrate gel and a denser layer of calcium hydroxide both of which can be useful in preventing corrosion of the steel that is under the layer of glass. The investigation reported here is directed at examining the condition of the surface and embedded cement before and after hydration occurs in a paste.

2. METHODS AND MATERIALS

Three types of testing in three different types of samples have been undertaken. Testing to determine the effects of the cementing reaction on the composition of the coating were undertaken using metal straps that were embedded in mortar.

Corrosion tests were undertaken with coated and uncoated smooth metal rods (corrosion coupons) that were exposed in an aggressive salt solution. Coated

samples included both glass enamel and glass enamel containing portland cement.

The bonding enamel fired onto the surface of the steel contains portland cement through its entire thickness. Only the cement exposed at the surface can react with water and hydrate. If the coating is crack and the embedded unreacted cement hydrates it can fill the crack and also raise the alkalinity of the interstitial water involved in the reaction. An examination of the self-healing properties of the coating was done using a metal wire that was coated in the same manner as the strap samples.

2.1 Examination of the Hydration Reaction.

In order to obtain samples of enamel-cement mixture after it was fired on to steel, the adhering hydrated cement and the coating after interaction with cement paste; strap-shaped metal samples were coated and cast into mortar cylinders and the cylinders were broken (Fig. 2).

Fig. 2. Photo of coated strap in mortar cylinder after breaking the cylinder by withdrawing the strap. Note the mortar still adheres to the coating.

The coating consisted of 0.2 mm of coating on a 2 mm thick, 25 mm wide strip of mild steel. Details on the preparation are presented in (Lynch et. al. 2007).Samples of reacted and unreacted coating for examination by XRD were obtained by chipping and scraping the coating off the samples that were in as coated condition or that were broken out of the hardened mortar. Pieces of the strap were also cut into samples that would allow them to be examined using optical and scanning electron microscopy.

The surface morphology of the test samples was characterized as to morphology using both optical microscopy and scanning electron microscopy. The optical imaging was done using a Nikon SMU-Z binocular microscope equipped with a CoolSNAPpro

Table 1. Comparison Of Average Bond Strengths

Treatment	Average Peak Force lbf (N)	Std. Deviation lbf (N)	Average Bond Strength psi (MPa)
Steel fiber embedded in mortar (Maage, 1978)	---	---	295.4 – 394.5 (2.04 – 2.72)
Steel rods, uncoated embedded in mortar	588.7 (2,618.2)	104.8 (466.2)	298.8 (2.06)
Enameled rods without portland cement embedded in mortar	786.4 (3,497.9)	121.6 (540.8)	391.6 (2.70)
Rods with enamel containing portland cement embedded in mortar	2500.9 (11,124.6)	52.9 (235.3)	1274.9 (8.79)

digital image acquisition system (Media Cybernetics). The electron microscopy was done using an Electroscan Environmental Scanning Electron Microscope (ESEM) Model 2020 with a lanthanum hexaboride (CeB_6) electron source and a gaseous secondary electron detector (GSED). The imaging conditions employed an accelerating voltage of 20 KeV and 1.81 mA, and approximately 5 Torr (666 Pa) water vapor in the sample chamber. The environmental gas was vaporized distilled water supplied via a digitally controlled needle valve assembly contained in a sealed located outside the sample chamber. Erlenmeyer flask Images of these samples were collected over a period of 30 seconds, and stored as 1 MB TIF files.

The crystal structure of the coating was determined using the Philips PW1800 Automated Powder Diffractometer system. The run conditions included use of CuKα radiation and scanning from 2 to 65 °2θ with collection of the diffraction patterns accomplished using PC-based Windows versions of Datascan (Materials Data, Inc.) and analysis using Jade.

2.2 Examination of the Corrosion Protection.

The goal of the testing was to provide conditions that would promote the mode of corrosion that would occur in carbonated (non-alkaline) portland cement concrete that was contaminated with chloride. The examination of corrosion phenomena in the bare rods, enameled rods and enameled rods with the portland cement addition was done by exposing sets of three identically prepared rods to a 3% sodium chloride solution in partly saturated sand. The pH of the wet, drained sand ranged from 6.0 to 6.5 and the temperature was maintained at 25 °C. Because of the typically high electrical resistance of the enamel, corrosion will only occur if a defect (or holiday) that exposed the metal rod was intentionally prepared in the enamel coating. Vitreous enamel typically has a volume resistivity of 1×10^{14} ohm·cm, so a perfect enamel surface is an insulator. Defects were prepared in each of the coated rods. All of the enameled rods were tested using the procedure outlined in ASTM C 876 and showed potentials more negative than -0.35 CSE (copper sulfate electrode) indicating corrosion was occurring. The test

rods were examined and photographed after 72 hours of salt water exposure and after 40 days. Data on surface pH were collected using colorimetric test strips.

2.3 Examination of Self-Healing Effects.

In order to determine if self-healing was occurring, specimens of 1.2-mm diam. steel wire mesh were enameled using a mixture of 50% glass frit and 50% portland cement (Fig. 3. Piece of wire were cut to approximately 8-mm length and examined using the SEM. Cracks were produced by bending the wire. Selected sections of cracked enamel were maintained in the wet condition and examine periodical for evidence of gel formation and crack-filling. The results were documented using SEM imaging.
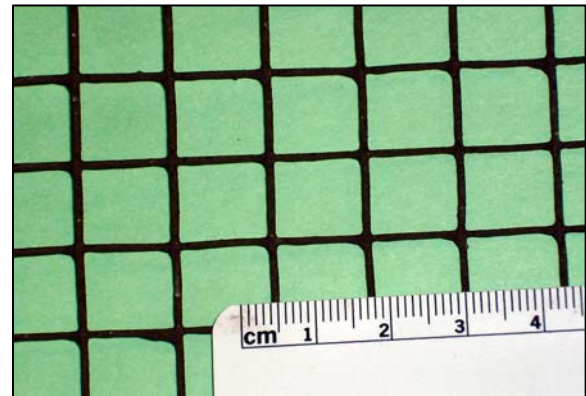

Fig. 3. Enameled welded wire mesh. This was prepared with a single application and single firing technique and produced no noticeable distortion of the mesh.

3. RESULTS

3.1 Investigation of the Hydration Reaction.

Figure 4 shows the surface of steel strap sample with the enamel chipped away to expose the glass-metal interface. The reaction of the glass with the underlying steel leaves a silica-rich layer on the metal surface. The bubble structure in the glass is evident.
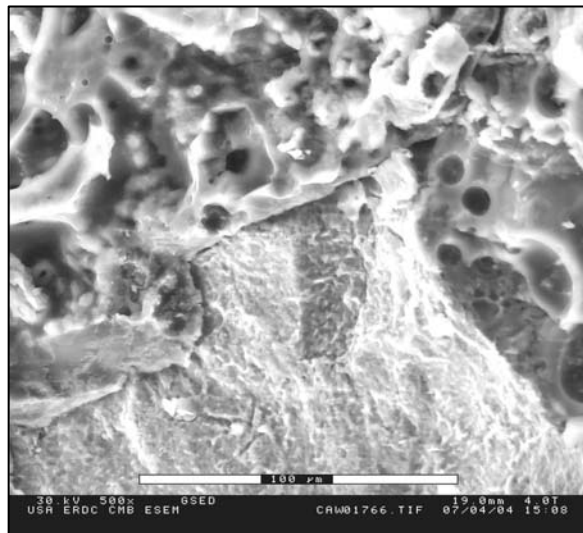
Fig. 4. Enamel chipped away to show the contact of the enamel and the underlying steel.

Figure 4 shows the hydrated portland cement grains on the surface of enamel. This portion of the coating was exposed to water but not embedded in the mortar. The cement hydrated forming portlandite that reacts to form calcite.
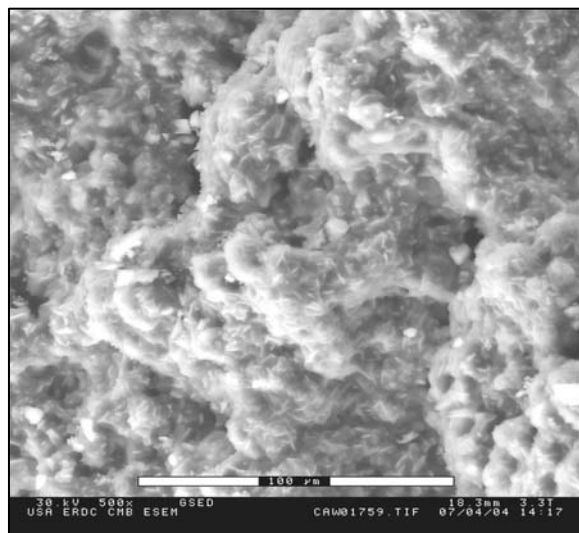

Fig.4 Surface of hydrated bonding enamel, crystalline material on the surface is reacted portland cement.

Figure 5 shows the surface of the bonding enamel that was removed from the mortar. The granular material adhering to the surface of the glass is mortar paste with quartz grains attached.

X-ray diffraction patterns obtained from ground samples of the unhydrated bonding enamel (Fig. 6), the hydrated enamel (Fig. 7) and enamel recovered from under the adhering mortar (Fig. 8) are shown below. The pattern from the unhydrated enamel shows unreacted cement and the portland cement contains all of the crystalline phases that would be associated with cement. None were altered in the firing process even though the enameling process requires that the material be maintained at approximately 850 °C for 5 to 20 minutes. Even gypsum (calcium sulfate dihydrate) did not decompose although it should lose attached water molecules at etemperatures above 70 °C (Deer, Howie and Zussman, 1962) and significantly dehydrate above 123 °C (Prasad, Pradhan and Gowd, 2001). The kinetics of dehydration are slow enough that all of the cement components survive. The sample of hydrated coated (Fig. 7) shows prominent peaks for calcite and ettringite indicating normal hydration reaction have occurred. The pattern for the coating with the adhering mortar shows added peak for quartz and both calcite and portlandite. This pattern is typical for hardened mortar made with quartz sand as fine aggregate.
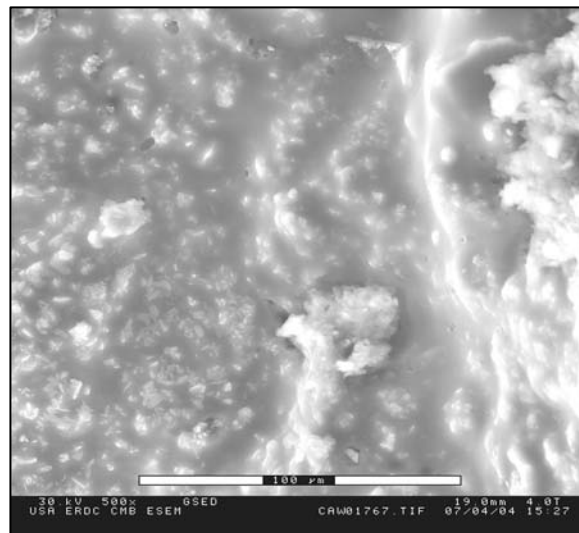
Fig. 5. Enamel with embedded cement grains and mortar attached to the surface.

3.2 Investigation of Corrosion on Coated and Uncoated Steel

Figure 9 shows the result of exposure of coated and uncoated steel test rods to a dilute solution for 40 days. The uncoated rod is badly corroded. The coated rod contained portland cement embedded in the enamel and the cement hydrated to produce a slightly rough surface. The glass-cement coating prevented contact with the salt solution and no corrosion occurred. Corrosion could only be produced is the enamel was purposely removed by drilling through the coating to expose the metal. When moistened the surface of the coating was alkaline (pH =~12) when tested using colorimetric techniques.
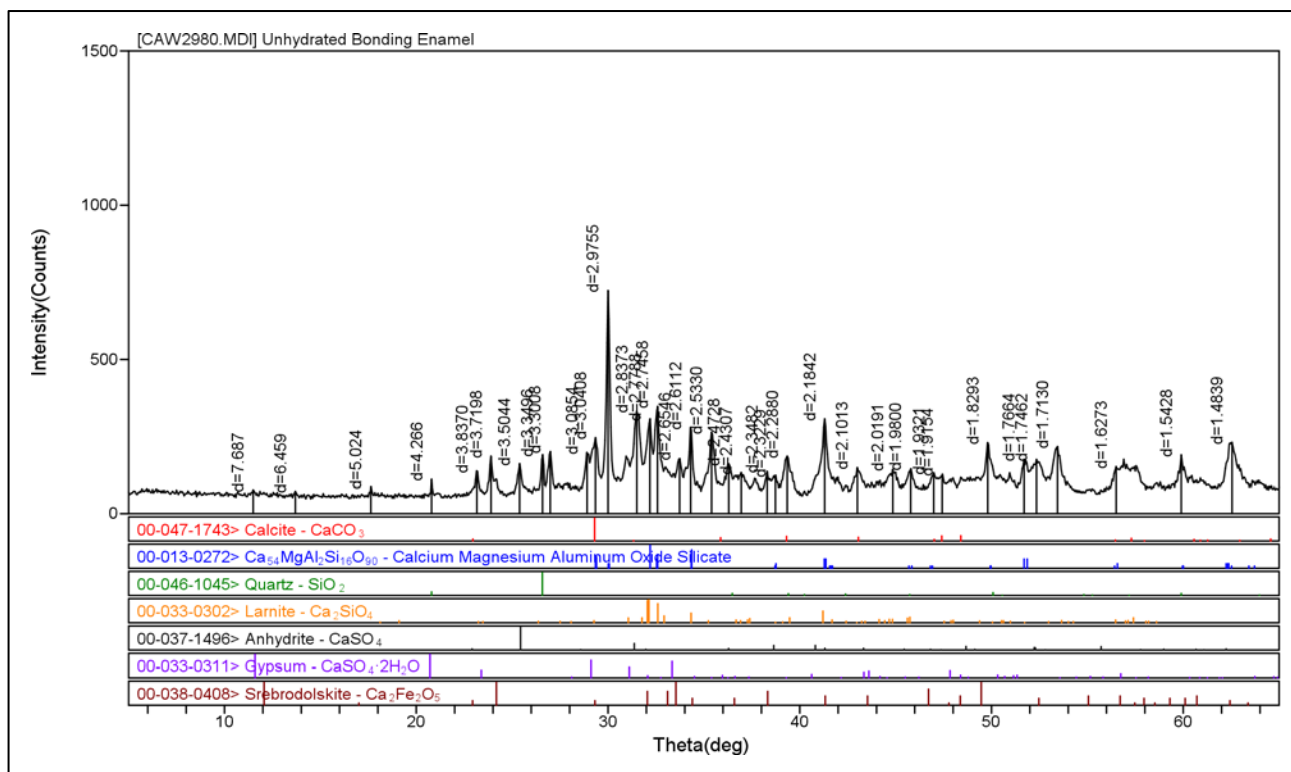
Fig. 6. X-ray diffraction pattern from vitreous enamel coating before hydration. Common crystalline products from portland cement are present.
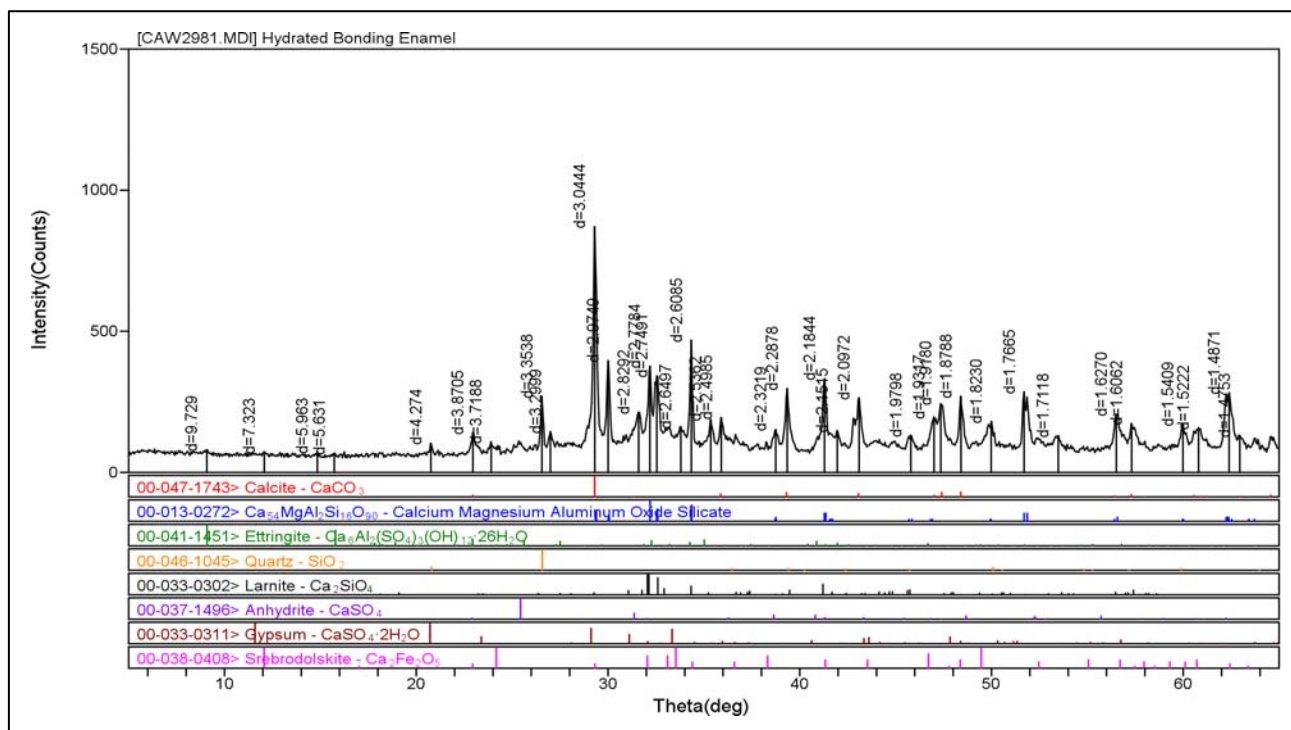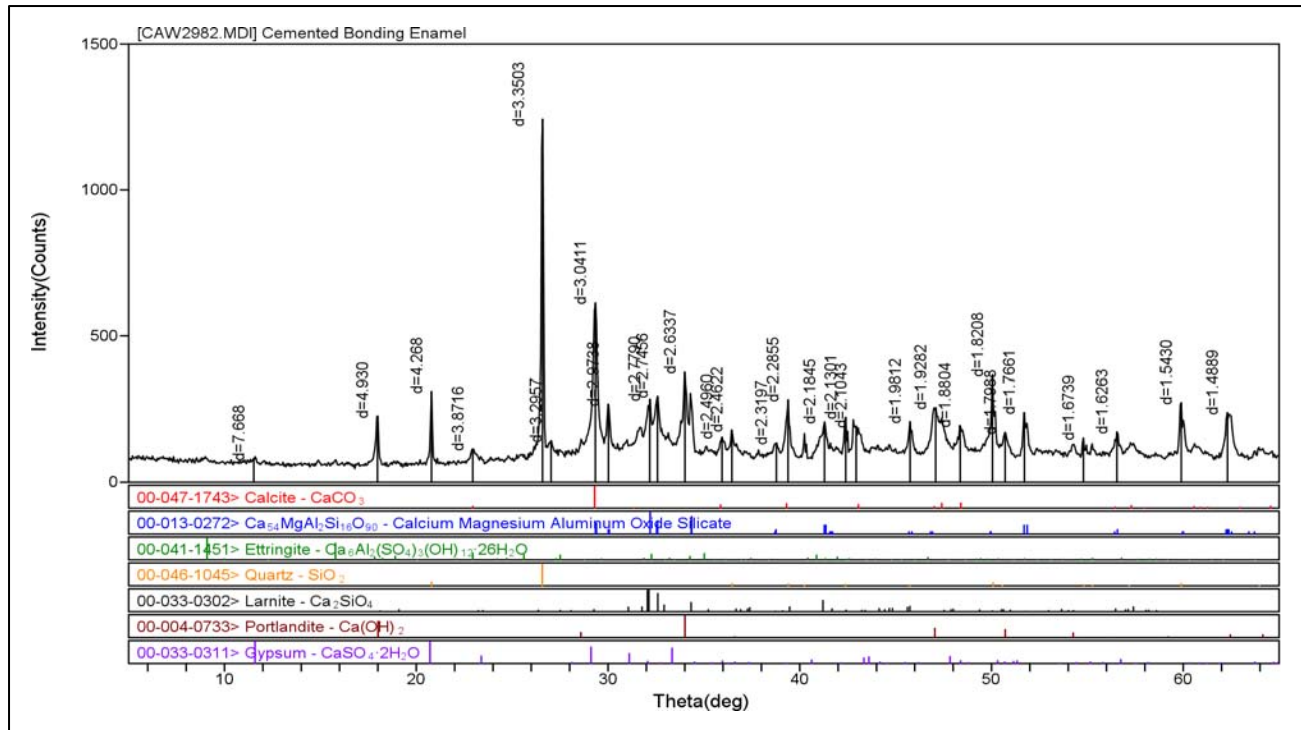

Fig. 7. X-ray diffraction pattern of coating after hydration.

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**Fig. 8. X-ray diffraction pattern for coating with adhering mortar.**

Fig. 9. Corrosion observed to uncoated (left) and coated test rods after 40-day exposure to a 3.5% NaCl solution. The dull surface of the coated rod is produced when the portland cement embedded in the glass hydrated.

3.3 Investigation of Self-healing Effects on Coated Steel

The glass coating containing portland cement is prepared by mixing portland cement with a fluid ground glass slip that is applied to the surface of the steel and fired on. The coating contains portland cement grains through its entire thickness. In undamaged glass only the portland cement grains on the surface can react with water to produce portland cement gel. Examination of the condition of coated steel wire after bending (to produce cracks in the coating) and moistening the cracked area showed that the embedded unreacted cement exposed in the crack would hydrate if wetted. Fine filled crack can be observed in the center of the field in Fig. 10.
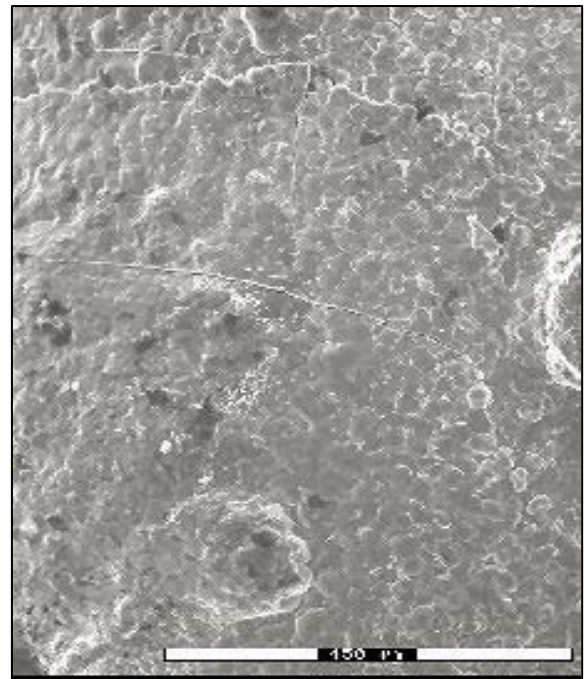
Fig. 10. Electron photomicrograph of glass coating after cracking and wetting the coating

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CONCLUSIONS

The investigation of composition and behavior of the composite portland cement vitreous enamel has shown the following:

a) The firing process used in enamel application does not alter the composition of the portland cement mix with the glass in the enamelling slip.

b) The portland cement exposed on the surface of the glass does hydrate when embedded in fresh mortar.

c) The glass enamel containing portland cement will protect the underlying reinforcing steel in an aggressive environment.

d) If the enamel coating is cracked the freshly exposed portland cement grains will react with any moisture in contact with them to produces a cement paste in the crack. Potentially this could be a desirable "self-healing" characteristic.

ACKNOWLEDGMENTS

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